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(54) Title: FISCHER-TROPSCH CATALYST WITH LOW SURFACE AREA ALUMINA, ITS PREPARATION AND USE THEREOF

(57) Abstract: A catalyst for use in a Fischer-Tropsch synthesis reaction which comprises cobalt supported on alumina. The alumina support has a specific surface area of less than 50m²/g or is at least 10% α -alumina.

FISCHER-TROPSCH CATALYST WITH LOW SURFACE AREA ALUMINA, ITS PREPARATION
AND USE THEREOF

The present invention relates to Fischer-Tropsch (F-T) catalysts, their use in F-T synthesis reactions, methods of their use and methods of their manufacture.

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Conversion of natural gas to liquid hydrocarbons ("Gas To Liquids" or "GTL" process) is based on a 3 step procedure consisting of: 1) synthesis gas production; 2) synthesis gas conversion by FT synthesis; and 3) upgrading of FT products (wax and naphtha/distillates) to final products such as naphtha, kerosene, diesel or other products, for example lube oil base.

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Supported cobalt catalysts are the preferred catalysts for the FT synthesis. The most important properties of a cobalt FT catalyst are the activity, the selectivity usually to C₅ and heavier products and the resistance towards deactivation. Known catalysts are typically based on titania, silica or alumina supports and various metals and metal oxides have been shown to be useful as promoters.

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A recent series of papers by Iglesia et al. including "Selectivity Control and Catalyst Design in the Fischer-Tropsch Synthesis: Sites, Pellets and Reactors" Advances in Catalysis, Vol. 39, 1993, p. 221-302, has given a description of the reaction network leading to various hydrocarbon products and a methodology to optimize catalyst properties towards the desired heavy hydrocarbons. The maximum C₅⁺ selectivity is obtained by designing catalyst pellets with optimum intraparticle diffusion resistance. This is achieved by increasing intraparticle diffusion resistance to the point where secondary chain building reactions of primary products (alpha-olefins) are maximized without inducing significant diffusion resistance on the reactants (H₂, CO) because this will lead to poor selectivity. This principle is shown to be generally applicable on all the supports mentioned above. By plotting different catalysts with different physical properties (particle size, porosity, cobalt loading, cobalt dispersion) a typical "volcano plot" is generated and the maximum C₅⁺ selectivity is found for intermediate values of

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a parameter " χ " which is a function of the parameters mentioned above and is a measure of the intraparticle diffusion resistance at a given set of reaction conditions.

Definition of χ :

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$$\chi = R_0^2 \varnothing \theta / r_p \quad (1)$$

where:

R_0 = Catalyst particle radius (m)

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\varnothing = Catalyst porosity

θ = Catalytic site density (sites/m²)

r_p = average pore radius (m)

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According to Iglesia the optimum value of χ for a typical set of FT reaction conditions (200°C, 20 bar, H₂/CO = 2.1, 50-60% conversion) is about 500-1000 × 10⁻¹⁶ m⁻¹, irrespective of the nature of the catalyst support used. From the definition of χ it appears that any of the parameters involved (particle radius, porosity, pore radius or site density) can be varied to achieve the desired value of χ . However, this is somewhat misleading due to the known relationship between specific surface area, pore radius and porosity (or specific pore volume). By introducing these relationships, it will be seen that χ can be described by the particle size, the cobalt loading, the cobalt dispersion and the porosity. Thus, it can be seen that χ is actually independent of pore radius and site density and is determined only by the volumetric transport parameter which is controlled solely by particle size, the cobalt loading, the cobalt dispersion and the porosity.

25

The following known equations are valid for an ideal cylindrical pore structure:

$$r_p = 2V_g / S_g \quad (2)$$

$$V_g = \varnothing / \rho_p \quad (3)$$

$$\rho_p = (1 - \varnothing) \rho_s \quad (4)$$

5 where

V_g = specific pore volume (cm^3/g)

S_g = specific surface area (m^2/g)

ρ_p = particle density (g/cm^3)

10 ρ_s = material density (g/cm^3)

The site density term in (1) (θ = Co sites/ m^2) can be expressed by:

$$\theta = \text{Co sites}/\text{m}^2 \text{ surface area} = X_{\text{Co}} D_{\text{Co}} A / S_g M_{\text{Co}} \quad (5)$$

15

where

X_{Co} = Total Co concentration in catalyst ($\text{g}_{\text{Co}}/\text{g}_{\text{cat}}$)

D_{Co} = Co dispersion (fraction of total Co exposed)

20 A = Avogadro number = $6.23 \cdot 10^{23}$ atoms/mole

M_{Co} = Co molecular weight = 58.9 g/mole

By combining equations (2)-(5) with (1) it can be shown that χ can be written as:

$$25 \quad \chi = R_0^2 X_{\text{Co}} D_{\text{Co}} A (1 - \varnothing) \rho_s / 2M_{\text{Co}} \quad (6)$$

It is apparent from (6) that χ actually is independent of pore radius and only depends on the volumetric density of sites in the free pore volume of the catalyst. It is also

clear that due to the second order dependency on particle size, the easiest way of controlling χ is to vary the particle size.

If a cobalt catalyst is to be used in a fixed-bed type reactor it is necessary to use particle sizes of 1 mm or larger in order to avoid unacceptable pressure drop over the reactor. However, the value of χ is then far too high to achieve optimum selectivity, due to high reactant diffusion resistance. This can to a certain extent be addressed by the use of so called eggshell or rim type catalysts where the active cobalt containing phase is located in a relatively thin region in the outer shell of the support. However, in slurry type reactors, it is necessary to employ much smaller particles, typically 10-100 μm . It is then easily seen that it will be extremely difficult to achieve χ values in the desired region. For example, a catalyst with 10 weight % cobalt loading, 5% Co dispersion, 50% porosity and 50 micron particles will have $\chi = 13 \times 10^{16} \text{ m}^{-1}$.

It should also be kept in mind that the parameters in eq. (6) can generally not be changed independently, i.e. the higher Co loading the more difficult it is to achieve a high dispersion. Moreover, the lower the porosity the more difficult it becomes to use a high cobalt loading. A combination of 20 weight% cobalt loading, 10% Co dispersion and 30% porosity gives a higher volumetric cobalt density than can be seen in any reference known to the applicants. The corresponding value of χ for a 50 μm particle (which is suitable for slurry reactor operation) will then be $75 \times 10^{16} \text{ m}^{-1}$, which is still far lower than the optimum value taught by Iglesia.

Thus, there is no apparent teaching for preparing high selectivity catalysts for use with small particle sizes, such as are encountered in slurry reactors.

The applicants have concluded a series of experiments to investigate the effect of χ on selectivity using a rhenium promoted cobalt on alumina support catalyst. These show only limited optimization potential by changing χ through changing the particle size. The results are shown in Figure 1. Figure 1 shows the effect χ on selectivity using

20%Co1%Re/ γ -Al₂O₃ catalyst (8% dispersion, 60% porosity, average particle size (microns): 46, 113, 225, 363, 638). Fixed bed reactor tests were conducted at: 200°C, 20 bar, H₂/CO = 2.1, 50-70% conversion, >24 h on stream. All data have been replicated 2 or more times.

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Iglesia suggests that the C₅+ selectivity can be increased by decreasing the relative density or reactivity of olefin hydrogenation vs. olefin readsorption sites. This effect is a direct consequence of the formulation of the reaction network. However, no guidance is given as to how this change can be built into a real catalyst.

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It is an object of the present invention to provide a F-T catalyst for use in slurry reactors with improved selectivity to C₅+ hydrocarbon.

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One of the requirements of a catalyst for use in a slurry reactor is that the particles of catalyst should retain their structural integrity. Catalysts which are supported on titania are relatively weak and though encouraging results have been achieved from the point of view of selectivity, there may be a tendency for titania-supported cobalt catalysts to disintegrate upon prolonged use. Alumina has an inherently stronger resistance against attrition and break-up of the catalyst particles than titania and is thus a more preferred support material from the point of view of mechanical properties.

20

According to one aspect of the present invention, there is provided a catalyst for use in a Fischer-Tropsch synthesis reaction which comprises cobalt supported on alumina, in which the alumina support has a specific surface area of <50m²/g preferably <30m²/g, but preferably not below 5m²/g.

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Preferably, the alumina is at least 50% alpha-alumina, with the remainder being gamma- and/or theta-alumina, preferably, predominantly theta-alumina. Preferably, it is at least 80% or even substantially pure alpha-alumina.

30

Preferably, the cobalt represents from 3 to 35% by weight of the catalyst, more preferably from 5 to 20% by weight. The catalyst may also include up to 2% by weight of rhenium, e.g. 0.25 to 1 % or 0.25 to 0.5% rhenium. Other known metallic promoters/dopants such as platinum, rhodium, iridium and palladium may also be included, preferably at the same levels, as well as oxide promoters/dopants such as rare earth oxides and alkali metal oxides.

According to another aspect of the present invention, there is provided a method of manufacturing a Fischer-Tropsch catalyst which comprises heat treating alumina particles at a temperature in the range of 700 to 1300°C for a period of between 1 and 15 hours; and impregnating the heat treated alumina particles with cobalt and any desired promoters/dopants. Preferably, the treatment temperature is in the range of 900 to 1200°C and the treatment period is between 5 and 10 hours.

The invention also extends to the use of a catalyst according to the first aspect of the invention in a F-T synthesis reaction. This may suitably be carried out in a slurry bubble column reactor.

The invention also extends to a method of converting natural gas to C₅+ hydrocarbons, which comprises; subjecting a natural gas feed stream to a reforming reaction to produce a synthesis gas feed stream of hydrocarbon and carbon monoxide; subjecting the synthesis gas feed stream to a Fischer-Tropsch synthesis reaction in the presence of a catalyst according to the first aspect; and separating a product stream including C₅+ hydrocarbons.

The method of depositing the active metal, the metallic promoters, the alkali and the rare earth oxide on the alumina support is not critical, and can be chosen from various methods well known to those skilled in the art. One suitable method that has been employed is known as incipient wetness impregnation. In this method the metal salts are dissolved in an amount of a suitable solvent just sufficient to fill the pores of the

- catalyst. In another method, the metal oxides or hydroxides are coprecipitated from an aqueous solution by adding a precipitating agent. In still another method, the metal salts are mixed with the wet support in a suitable blender to obtain a substantially homogenous mixture. In the present invention, if incipient wetness impregnation is used, the catalytically active metal and the promoters can be deposited on the support using an aqueous or an organic solution. Suitable organic solvents include, for example, acetone, methanol, ethanol, dimethyl formamide, diethyl ether, cyclohexane, xylene and tetrahydrofuran.
- 10 Suitable cobalt compounds include, for example, cobalt nitrate, cobalt acetate, cobalt chloride and cobalt carbonyl, with the nitrate being the most preferable when impregnating from an aqueous solution. Suitable rhenium compounds include, for example, rhenium oxide, rhenium chloride and perrhenic acid. Perrhenic acid is the preferred compound when preparing a catalyst using an aqueous solution. Suitable platinum, iridium and rhodium compounds include, for example, nitrates, chlorides and complexes with ammonia. Suitable alkali salts for incorporating the alkali into the catalyst include, for example, the nitrates, chlorides, carbonates, and hydroxides. The rare earth oxide promoter can suitably be incorporated into the catalyst in the form, for example, of the nitrate or chloride.
- 20 After aqueous impregnation, the catalyst is dried at 110°C to 120°C for 3 to 6 hours. When impregnating from organic solvents, the catalyst is preferably first dried in a rotary evaporator apparatus at 50°C to 60°C under low pressure, then dried at 110°C to 120°C for several hours longer.
- 25 The dried catalyst is calcined in air by slowly increasing the temperature to an upper limit of between 200°C and 500°C, preferably between 250°C and 350°C. The rate of temperature increase is preferably between 0.5°C and 2°C per minute, and the catalyst is held at the highest temperature for a period of 1 to 24 and preferably 2 to 16 hours.
- 30 The impregnation procedure is repeated as many times as necessary to obtain a

catalyst with the desired metals content. Cobalt, rhenium, alkali and the rare earth oxide promoter, if present, can be impregnated together, or in separate steps. If separate steps are used, the order of impregnating the active components can be varied.

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Before use, the calcined catalyst is preferably reduced with hydrogen. This can be suitably carried out by flowing hydrogen at a space velocity of at least $1000 \text{ Ncm}^3/\text{g}$. The temperature is slowly increased from ambient to a maximum level of 250°C to 450°C , preferably between 300°C and 400°C , and maintained at the maximum

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temperature for about 1 to 24 hours, more preferably 5 to 16 hours.

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The reactor used for the synthesis of hydrocarbons from synthesis gas can be chosen from various types well known to those skilled in the art, for example, fixed bed, fluidized bed, ebullating bed or slurry. The catalyst particle size for the fixed or ebullating bed is preferably between 0.1 and 10 mm and more preferably between 0.5 and 5 mm. For the other types of operations a particle size between 0.01 and 0.2 mm is preferred.

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The synthesis gas is a mixture of carbon monoxide and hydrogen and can be obtained from any source known to those skilled in the art, such as, for example, steam reforming of natural gas or partial oxidation of coal. The molar ratio of $\text{H}_2:\text{CO}$ is preferably between 1:1 to 3:1; and more preferably between 1.5:1 to 2.5:1. Carbon dioxide is not a desired feed component for use with the catalyst of this invention, but it does not adversely affect the activity of the catalyst. All sulfur compounds must, on

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the other hand, be held to very low levels in the feed, preferably below 100 ppb.

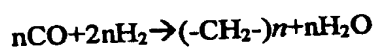
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The reaction temperature is suitably between 150°C and 300°C , and more preferably between 175°C and 250°C . The total pressure can be from atmospheric to around 100 atmospheres, preferably between 1 and 50 atmospheres. The gaseous hourly space velocity, based on the total amount of synthesis gas feed, is preferably between 100

and 20,000 cm³ of gas per gram of catalyst per hour; and more preferably from 1000 to 10,000 cm³/g/h, where gaseous hourly space velocity is defined as the volume of synthesis gas (measured at standard temperature and pressure) fed per unit weight of catalyst per hour.

5

The reaction products are a complicated mixture, but the main reaction can be illustrated by the following equation:

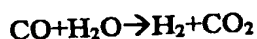


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where $(-\text{CH}_2)_n$ represents a straight chain hydrocarbon of carbon number n. Carbon number refers to the number of carbon atoms making up the main skeleton of the molecule. In F-T synthesis, the products are generally either paraffins, olefins, or alcohols. Products range in carbon number from one to 50 or higher.

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In addition, with many catalysts, for example, those based on iron, the water gas shift reaction is a well known side reaction:



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With cobalt catalysts the rate of this last reaction is usually very low.

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The hydrocarbon products from Fischer-Tropsch synthesis are distributed from methane to high boiling compounds according to the so called Schulz-Flory distribution, well known to those skilled in the art. The Schulz-Flory distribution is expressed mathematically by the Schulz-Flory equation:

$$W_n = (1-\alpha)^2 n \alpha^{n-1}$$

where n represents carbon number, α is the Schulz-Flory distribution factor which represents the ratio of the rate of chain propagation to the rate of chain propagation plus the rate of chain termination, and W_n represents the weight fraction of product of carbon number n . This equation shows that an increased α results in a higher average carbon number of the products. Higher α values are desirable when heavier products, such as diesel fuel, are relatively more valuable than lighter products, such as naphtha and light gases.

The invention is therefore concerned with the preparation and use in FT synthesis of a cobalt supported catalyst on low surface area alumina for optimizing C_5+ selectivities. This is preferably achieved by heat treatment of high surface area aluminas to achieve the desired surface areas, but it is understood that any means of achieving materials with such properties are covered by the invention. Another advantage of the invention is the surprisingly high activity and high resistance towards deactivation of the described materials.

The invention describes catalytic materials that can be used in any type of FT reactor that is suitable for synthesis of heavy hydrocarbons (e.g. fixed-bed and slurry reactors). It should be understood that any combination of cobalt and suitable promoters (such as Re, Pt or other suitable components) will benefit from the use of the low surface area alumina supports, including unpromoted cobalt catalysts.

The catalysts of the invention provide a way to achieve high C_5+ selectivities at low values of χ , i.e. at low values of intraparticle diffusion resistance. Thus, these catalysts circumvent the limitations imposed by the teaching of Iglesia. It has been discovered that cobalt supported on low surface area alumina can achieve substantially improved C_5+ selectivities in FT synthesis compared to high surface area alumina, even at low values of χ . This has been achieved by heat treatment of high surface area aluminas to achieve the desired surface areas. The results of tests conducted indicate that the

increase in C₅+ selectivity may be at least partially attributable to a reduced olefin hydrogenation activity relative to the main FT synthesis activity.

5 It has also been discovered that these catalysts, in spite of the low surface area available for impregnation of active components have an activity which is higher than comparable high surface area (HSA) catalysts at conditions which simulate high conversion in a slurry bubble column reactor (i.e. at high and uniform water partial pressures). In fact, the low surface area catalyst activity is close to the activity of a high surface area catalyst with higher Co loading.

10 In the low surface area catalyst, the loss of activity per unit time is not affected but there is a reversible step change upwards in activity for the low surface area catalyst which is not observed for the HSA catalyst.

15 A further benefit over known technology is that since the composition of the wax is displaced towards the heavy side (higher α value), this leads to an increase in the middle distillate yield or lube oil base when the wax is hydrocracked or hydroisomerised in a downstream process. The consequence of this in a total GTL process is that the recycle of unconverted gas back to the natural gas reforming section
20 can be reduced, the overall efficiency of the process can be increased (i.e. CO₂ emissions will be reduced) and the oxygen consumption can be reduced. Still further, it has been discovered that the catalysts according to the invention show a reduced water-gas-shift activity, leading to decreased undesired CO₂ production.

25 The invention may be carried into practice in various ways and will now be illustrated by the following examples.

In the drawings:

Figure 1 is a graph showing the effect of χ on C₅+ selectivity;

30 Figure 2 is a graph showing the effect of support surface area on C₅+ selectivity;

Figure 3 is a graph showing C₅+ selectivity as a function of % α Al₂O₃ in the support;

Figure 4 is a graph showing the effect of χ on C₅+ selectivity using Al₂O₃ supported Co catalysts;

Figure 5 is a graph showing the effect of cobalt loading on C₅+ selectivity using Al₂O₃ supported cobalt catalysts;

Figure 6 is a graph showing the effect of cobalt loading on catalyst productivity using Al₂O₃ supported cobalt catalysts;

Figure 7 is a graph showing propene and propane selectivity as a function of support surface area; and

Figures 8 and 9 are graphs showing respectively propane and propene selectivity as a function of χ for Al₂O₃ supported Co catalysts.

Example 1. Catalyst preparation

The catalysts were prepared as follows: A solution was prepared by dissolving a given amount of cobalt nitrate, Co(NO₃)₂·6H₂O and in some of the catalysts also perhenic acid, HReO₄ or tetra amin platinum nitrate, Pt(NH₃)₄(NO₃)₂ in a given amount of distilled water. The total solution was added with stirring to a given amount of Condea Puralox SCCa 45/190 alumina treated in air at different temperatures prior to impregnation, and the amount of solution added to the alumina was sufficient to achieve incipient wetness. The prepared catalysts were dried for 3 hours in an oven at a temperature of 110°C. The dried catalysts were then calcined in air by raising its temperature at a heating rate of 2 °/minute to 300°C and holding at this temperature for 16 hours. After calcination the catalysts were screened to the desired particle size. The amounts used in preparation and the content of the prepared catalysts are given in table 1a.

Table 1a. Catalyst preparation data of Al₂O₃ supported catalysts. Catalysts written in bold are according to the invention. Other materials are included for comparison.

Cat.	Co(NO ₃) 6H ₂ O (g)	HReO ₄ (g)	Pt(NH ₃) ₄ (NO ₃) ₂ (g)	Water (ml)	Al ₂ O ₃ (g)	Al ₂ O ₃ **** treatment (°C)	Catalyst composition (%)	Particle size (microns)
1	1077.93	17.93		1 070	826***	500	20%Co-1%Re	38-53
2	17.18	0.23		30	25	500	12%Co-0.5%Re	53-75
2b	11.49	-		21	17	500	12%Co	53-90
2c	133.39	-			108	500	20%Co	53-90
2d	130.83	2.17			105	500	20%Co-1%Re	53-90
3	16.93	0.23		22	25	1 100	12%Co- 0.5%Re	53-90
4	11.40	0.16		12	17	1 150	12%Co- 0.5%Re	53-90
4b	16.95	-		18	25	1 150	12%Co	53-90
5	2.61	0.04		7	10	1 150	5%Co- 0.25%Re	53-90
6	4.31	0.08		7	10	1 150	8%Co-0.4%Re	53-90
7	5.52	0.09		7	10	1 150	10%Co- 0.5%Re	53-90
8*	62.68	1.05		38	50	1 150	20%Co-1%Re	53-90
9	n.a.	n.a.		n.a.	10 000	500	20%Co-1%Re**	38-53
10								75-150
11								150-300
12								300-425
13								425-850
13b	10.16	0.14		9	15	1 150	12%Co- 0.5%Re	75-150
13c	10.16	0.14		9	15	1 150	12%Co- 0.5%Re	150-300
13d	10.16	0.14		9	15	1 150	12%Co- 0.5%Re	425-850

14	16.89	-	0.17	18	25	1 150	12%Co-0.3%Pt	53-90
15	16.89	-	0.17	30	25	500	12%Co-0.3%Pt	53-90
16	271.41	3.73		340	400	1130	12%Co-0.5%Re	38-53

*: Two-step impregnation to achieve 20%Co by incipient wetness.

**: Catalysts also containing 1% rare earth oxide (impregnated as $\text{La}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)

***: Condea Catapal support.

- 5 ****: The Al_2O_3 treatment temperature was gradually increased to the desired temperature over a period of 6 hours and then kept at the desired temperature for 10 hours.
- Catalysts 9-13 are different particle sizes of the same catalyst, of which the particle sizes are made by tabletising the powder before crushing and screening. The catalyst
- 10 (2 x 5 kg) was prepared by incipient wetness in a mixer, drying at 120°C for 2 hours and calcining at 300°C for 3 hours.

Example 2. Cobalt catalysts supported on high surface area alumina with varying particle size

- 15 Catalysts 9-13 in Table 1 were tested in an isothermal fixed-bed microreactor. The reactor was 25 cm long and had an inner diameter of 1 cm. Each catalyst was given a pretreatment consisting of reduction by passing hydrogen over the catalysts while heating the catalyst at a rate of 1°C/minute to 350°C and maintaining this temperature
- 20 for 16 hours at a pressure of 1 bar. In the tests, synthesis gas consisting of 2.1:1 $\text{H}_2:\text{CO}$ (+3 vol% N_2) was passed over 1-2 g of the catalyst diluted 1:5 with SiC at 20 bar at the desired temperature and space velocity. The space velocity was usually varied to keep the CO conversion between 40 and 70%. Products from the reactor were sent to a gas chromatograph with FID and TCD detectors for analysis, and
- 25 methane analysed on both detectors was used as a link in the calculations.

In order to investigate the influence of χ on C5+ selectivity, catalysts 9-13 were tested under the same reaction conditions as employed by Iglesia *et al.*

5 The results are given in Table 1b and illustrated graphically in Figure 1 and compared to the results of Iglesia *et al.* Figure 1 shows the effect of χ on C5+ selectivity using 20%Co1%Re-1RE/ γ -Al₂O₃ catalyst (8% dispersion, 60% porosity, average particle size (microns): 46, 113, 225, 363, 638).

10 The sharp decrease in C5+ selectivity at χ - values above ca. $1000 \cdot 10^{16} \text{ m}^{-1}$ is caused by intraparticle diffusion limitations for H₂ and CO, as explained by Iglesia *et al.* However, in the present context it is more important to notice that the C5+ selectivity of high surface area alumina-supported catalysts can not be increased significantly by variation of χ (particle size) from low ($<100 \cdot 10^{16} \text{ m}^{-1}$) to intermediate values (500-
15 $1000 \cdot 10^{16} \text{ m}^{-1}$) and other methods are thus evidently needed to increase the C5+ selectivity of alumina supported Co catalysts.

Table 1b. Properties and results from catalytic tests of materials described in table 1. Reaction conditions: Fixed-bed reactor at 200°C, 20 bar, feed $H_2/CO = 2.1$, 50-70% conversion, >24 hrs onstream

Cat.	Composition (wt%)	Support treatment temp. (°C)	Alumina phase (% α)	Surface area (m^2/g)	Porosity	Co dispersion (%)	Mean particle size (microns)	χ_{m-1} ($\times 10^{16}$)	GHSV ²⁾ (h^{-1})	CO conv. (%)	Reaction rate ³⁾ (g/g/h)	Selectivity ¹⁾ (%)		
												CH ₄	C ₂ -C ₄	C ₅ +
9	20%Co - 1%Re ¹⁾	500	0	182	0.60	8	46	29	2 650	57	0.3	6	10.4	83.5
10	20%Co - 1%Re ¹⁾	500	0	182	0.60	8	112	177	2 380	57	0.27	6.1	10.8	83.1
11	20%Co - 1%Re ¹⁾	500	0	182	0.60	8	225	707	2 500	62	0.31	5.9	9.8	84.2
12	20%Co - 1%Re ¹⁾	500	0	182	0.60	8	363	1 836	2 750	63	0.34	7.5	9.9	82.7
13	20%Co - 1%Re ¹⁾	500	0	182	0.60	8	638	5 678	3 300	53	0.35	12.9	8.8	78.3

¹⁾ Catalysts containing also 1% rare earth oxide (La₂O₃).

²⁾ Carbon selectivity, CO₂ free basis. (< 1%CO₂ in all experiments)

³⁾ Space velocity: Ncm³ (H₂+CO+inerts)/g catalyst/hour. (3 vol% inerts (N₂) were used in all tests)

⁴⁾ g C₁+hydrocarbons per g of catalyst per hour

Example 3. Cobalt catalysts supported on alumina with different surface area and phase composition

5 Alumina supports with different surface area and alumina phase composition were prepared by heat treatment at different temperatures as described in Example 1. The catalysts also contained varying amounts of cobalt and promoters. The catalysts were tested in a fixed-bed reactor using the same equipment and procedures as described in Example 2. The results for all of the catalysts are shown in Table 2 and illustrated in
10 Figures 2, 3 and 4.

Figures 2 and 3 show the C5+ selectivity for all of the catalysts with $\chi < 150 \cdot 10^{16} \text{ m}^{-1}$ (i.e. all catalysts with small particles) as a function of support surface area or α - alumina content. Although there is some apparent spread in the data, it is quite clear
15 that the low surface area / high α -alumina catalysts show significantly higher C5+ selectivities than high surface area γ -alumina supported catalysts. It is also evident that the effect is more significant at surface areas below ca. 50 m²/g and α - alumina content above ca. 10%.

20 Note also that the Schulz-Flory growth parameter (α) is increased for catalysts using low surface area alumina with a high content of α - alumina (see catalyst 2,3 and 4 in Table 2). The increase from α from 0.92 to 0.94 gives an increase in wax (C19+) yield (in % of the total hydrocarbon production) of more than 10% units (from below 50% to above 60%).

25 Figure 4. shows a plot of C5+ selectivity as a function of χ for catalysts from Table 2. It is evident that two parallel curves arise from the data, one for high surface area γ -alumina supports and another for low surface area alumina with a high content of α -alumina. The latter shows on the average 4-6 % units higher C5+ selectivity than the

former for all values of χ . The apparent spread in data in Figures 2-4 will be further explained by Examples 4 and 5.

Table 2. Properties and results from catalytic tests of materials described in table 1. Reaction conditions: Fixed-bed reactor at 210°C, 20 bar, feed H₂/CO = 2.1, 40-70% conversion, about 100 hrs on stream

Cat.	Composition (wt%)	Support treatment temp. (°C)	Alumina phase (% α)	Surface area (m ² /g)	Porosity	Co dispersion (%)	Mean particle size (microns)	χ _m (x10 ¹⁶)	GHSV ²⁾ (h ⁻¹)	CO conv. (%)	Reaction rate ³⁾ (g/g/h)	Selectivity ¹⁾ (%)			α
												CH ₄	C ₂ -C ₄	C ₅ +	
1	20%Co - 1%Re	500	0	183	0.65	8.3	46	27	7100	43	0.61	8.8	10.1	81.1	---
2	12%Co - 0.5%Re	500	0	191	0.75	11.2	64	30	5100	49	0.50	9.1	9.2	81.8	0.92
2b	12%Co	500	0	191	0.75	9.8	72	33	4700	46	0.43	9.4	10.1	80.9	---
2c	20%Co	500	0	191	0.75	7.5	72	43	6200	45	0.55	9.7	10.8	79.5	---
2d	20%Co - 1%Re	500	0	191	0.75	10.5	72	43	8400	46	0.77	9.3	9.9	81.2	0.92
3	12%Co - 0.5%Re	1100	7	66	0.64	12.4	72	60	5500	50	0.54	8.4	8.7	83.0	0.94
4	12%Co - 0.5%Re	1150	86	16	0.24	10.2	64	83	3900	55	0.43	6.8	5.4	87.8	---
4a	12%Co - 0.5%Re	1150	86	16	0.24	10.2	84	139	4300	53	0.45	6.0	5.3	88.7	---
4b	12%Co	1150	86	13	0.19	6.8	72	74	3100	48	0.30	8.2	8.0	83.8	---
5	5%Co - 0.25%Re	1150	86	13	0.19	8.5	72	38	1700	45	0.15	7.5	6.3	86.2	---
6	8%Co - 0.4%Re	1150	86	13	0.19	8.6	72	62	2900	45	0.26	6.6	5.4	88.0	---
7	10%Co - 0.5%Re	1150	86	13	0.19	9.6	72	87	3700	48	0.36	6.8	6.1	87.1	---
8	20%Co - 1%Re	1150	86	16	0.24	5.7	72	98	4600	47	0.43	7.6	6.9	85.5	---
9	20%Co - 1%Re	500	0	182	0.60	8	46	29	4800	54	0.51	6.8	9.4	83.8	---
10	20%Co - 1%Re	500	0	182	0.60	8	112	177	3800	55	0.41	7.1	9.7	83.1	---
11	20%Co - 1%Re	500	0	182	0.60	8	225	707	4500	56	0.49	7.1	8.1	84.8	---
12	20%Co - 1%Re	500	0	182	0.60	8	363	1836	5000	62	0.62	10.4	8.1	81.5	---
13	20%Co - 1%Re	500	0	182	0.60	8	638	5678	4500	56	0.50	16.8	8.6	74.6	---
13b	12%Co - 0.5%Re	1150	86	7	0.11	7	113	207	3000	52	0.31	6.9	4.8	88.3	---
13c	12%Co - 0.5%Re	1150	86	6	0.11	6.6	225	781	3000	49	0.29	6.7	4.9	88.4	---
13d	12%Co - 0.5%Re	1150	86	7	0.08	7.7	613	6978	3400	49	0.34	13.4	6	80.6	---
14	12%Co-0.3%Pt	1150	86	13	0.19	7.7	72	84	3400	51	0.34	7.3	6.8	85.9	---
15	12%Co-0.3%Pt	500	0	191	0.75	8.8	72	30	4300	46	0.39	10.3	10.4	78.3	---

¹⁾ Catalysts containing also 1% rare earth oxide (La₂O₃.)²⁾ Carbon selectivity, CO₂ free basis. (< 1%CO₂ in all experiments)³⁾ Space velocity: Ncm³ (H₂+CO+inerts)/g catalyst/hour. (3 vol% inerts (N₂) were used in all tests)⁴⁾ g C₁+ hydrocarbons per g of catalyst per hour⁵⁾ Schultz-Flory chain propagation probability, measured in the C₃₀-C₅₀ range.⁶⁾ The CO dispersion has been measured by H₂-chemisorption for catalyst 9-13.

The CO dispersion for all other catalysts has been calculated by assuming the same site time yield as for catalyst 9-13.

Example 4. The effect of cobalt loading on alumina with different surface area and phase composition

5 The tests in Example 4 were fixed bed reactor tests at: 210°C, 20 bar, $H_2/CO = 2.1$, 45-55% conversion, ca. 100 h on stream.

10 The results indicate that there is an optimum loading of cobalt for a given alumina surface area. A more thorough examination of the results in Example 3 shows that some of the low C5+ selectivities for low surface area / high α - alumina supports are caused by too high loading of cobalt. This is illustrated in Figures 5 and 6. Figure 5 shows the effect of cobalt loading on C5+ selectivity and Figure 6 the effect on catalyst productivity using Al_2O_3 supported cobalt catalysts with different surface area / α -alumina content.

15 At 20% Co loading, there is a smaller gain in C5+ selectivity by using low-surface area / high α -alumina support (Figure 5). This is also clearly shown by examining the influence of Co loading on catalyst activity, as illustrated by the hydrocarbon production rate at these reaction conditions (Figure 6). In spite of the much lower surface area and pore volume of the catalysts according to the invention, the cobalt
20 utilisation is as good as for high surface area supports up to about 12% Co, after which it is apparent that the support can not effectively disperse the additional active metal.

25 However, the results are not intended to limit the invention to Co loadings below 12%, but merely to illustrate that there is an optimum level for each set of support properties. It is well known that the accommodation of active metal in supports can be varied and optimised by the method of impregnation, the type of cobalt precursor, the solvent used, the number of impregnation steps and the conditions for pretreatment of the catalyst to mention only a few.

Example 5. The effect of metal promoters

Although the results show a marked effect of surface area / α -alumina content for all of the catalysts, it is clear that there is synergy between the use of a metal promoter such as Re or Pt and the support properties. This is illustrated in Table 3, showing that the effect of low surface area / high α - alumina supports is clearly larger for the Pt and Re promoted catalysts compared to the unpromoted catalyst.

In order to make sure that the observed effect of promoters were not caused by secondary factors (χ) through the higher activity (dispersion) of these catalysts, experiments with Re promoted catalysts with lower Co loading and thus lower activity (and χ) were also performed. The results are given in Table 4, showing the positive effect of Re for catalysts with virtually constant activity (and χ - value).

Table 3. Difference in C5+ selectivity ($\Delta C5+$) between low surface area / high α -alumina and high surface area / γ -alumina based Co catalysts, with and without promoter. Catalyst sample numbers refer to Tables 1 and 2. Fixed bed reactor tests at: 210°C, 20 bar, $H_2/CO = 2.1$, 45-55% conversion, ca. 100 h on stream).

Catalysts (no.)	$\Delta C5+$ (%)
12Co (2b / 4b)	3.5
12Co0.5Re (2 / 4)	6.0
12Co0.3Pt (15 / 14)	7.6

Table 4. Reaction rate and C₅+ selectivity for catalysts supported on low surface area / high α - alumina with near-constant χ . Catalyst sample numbers refer to Table 1 and 2. Fixed bed reactor tests at: 210°C, 20 bar, H₂/CO = 2.1, 45-55% conversion, ca. 100 h on stream).

Cat.	Composition (wt%)	χ (m ⁻¹ x 10 ¹⁶)	Reaction rate (gHC/gcat/h)	Select. C ₅ + (%)
4b	12%Co	74	0.30	83.8
4	12%Co - 0.5%Re	83	0.43	87.8
6	8%Co - 0.4%Re	62	0.26	88.0
7	10%Co - 0.5%Re	87	0.36	87.1

Example 6. Water-gas shift activity

10

The water gas shift reaction ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$) is generally an unwanted side reaction to the main hydrocarbon synthesis formation. The water gas shift activity of the catalysts was tested by adding water (steam) to the feed in fixed-bed catalyst testing experiments otherwise similar to the experiments described in Example 2. This

15

has the advantage that the water partial pressure is higher and more uniform over the reactor and thus facilitates interpretation of the data.

Typical results for catalysts with low surface area / high α - alumina and high surface area / γ - alumina are shown in Table 5.

20

Although most cobalt catalysts have relatively low water gas shift activity, the results show that the catalysts according to the invention have still significantly lower (a factor of 2) CO₂ formation rates compared to catalysts supported on high surface area / γ - alumina.

5

Table 5. CO₂ selectivity for low surface area / high α - alumina and high surface area / γ - alumina based Co-Re catalysts. Catalyst sample numbers refer to Table 1 and 2. Fixed bed reactor tests at: 210°C, 20 bar. Feed composition (molar): 50.5% H₂, 24% CO, 22-23% H₂O, balance N₂, 40-50% conversion, 100-200 h on stream).

10

Cat.	Composition (wt%)	Support surface area (m ² /g)	% α - Al ₂ O ₃	CO ₂ select. (%)	CO ₂ formation rate (mmole / g _{cat} / h)
2	12%Co - 0.5%Re	191	0	0.56	0.156
4	12%Co - 0.5%Re	16	86	0.28	0.087

Example 7. Slurry reactor experiments

15

A catalyst according to the invention was also tested in slurry reactor in order to verify the selectivity advantage also under the conditions typical of such reactors. Results are shown in Table 6.

20

At virtually identical reaction conditions, the low surface area / high α - alumina supported catalyst show almost 7% increase in C5+ selectivity (compared to a typical high surface area / γ - alumina based catalyst), which is even more significant than

found in the fixed-bed reactor tests. The slurry reactor tests also confirm the difference in CO₂ selectivities as described in Example 6.

5 Table 6. Results from tests of Al₂O₃ supported Co catalysts (38-53 micron particles) in a 2 L stirred slurry reactor (CSTR). T = 220°C, P = 20 bar, feed H₂/CO = 2.0, 3% inerts (N₂) in feed. Results after > 100 h on stream.

Catalyst	Catalyst surface area (m ² /g)	CO conv. (%)	Selectivity (%C, CO ₂ free basis)			CO ₂ Selectivity (%)
			CH ₄	C ₂ -C ₄	C ₅ +	
20%Co-1%Re-1%RE*	140	77.4	8.3	7.8	83.9	2.7
12%Co-0.5%Re	25	77.7	5.3	3.8	90.8	1.1

* RE = Rare earth oxide (La₂O₃)

10 Example 8. The effect of water

The following example will illustrate that the positive influence of the invention on C₅+ selectivity is not dependent on the level of water concentration (steam partial pressure) in the reactor. Water is a product of the Fischer-Tropsch reaction and its partial pressure in the reactor will therefore be dependent on the conversion level. The following experiments were carried out in order to investigate the effect of conversion on selectivity for a catalyst representative of the invention and a comparative sample. In addition, experiments with addition of water (steam) to the reactor were carried out to further probe the effect of water. The experiments were carried out in a fixed-bed reactor using the same experimental procedures as described in Example 2, apart from

the addition of water and the deliberate variation of space velocity to influence conversion levels. The results are shown in Table 7.

5 It is evident that the effect of using low surface area / high α - alumina supports is independent on water partial pressure.

10 Table 7. The effect of water partial pressure on C5+ selectivity for low surface area / high α - alumina and high surface area / γ - alumina based Co-Re catalysts. Catalyst sample numbers refer to Table 1 and 2. Fixed bed reactor tests at: 210°C, 20 bar, H₂ /CO = 2.1, 500-600 h on stream.

Cat. No.	Catalyst descr.	CO conversion (%)	Inlet H ₂ O partial pressure (bar)	Average H ₂ O partial pressure (bar)	C ₅ + selectivity (%)	Δ C ₅ + Selectivity ¹⁾ (%)
4	12%Co - 0.5%Re 16 m ² /g 86% α - alumina	24	0	0.9	86.4	5.4
		50	0	2.2	88.4	4.6
		76	0	4.2	90.0	5.3
		30	4.6	5.8	91.4	5.6
2	12%Co - 0.5%Re 191 m ² /g 0% α - alumina	21	0	0.8	81.0	---
		50	0	2.2	83.8	---
		74	0	4.0	84.7	---
		22	4.6	5.3	85.8	---

¹⁾ C₅+ selectivity advantage of catalyst 4 compared to catalyst 2 at the same conditions

Example 9. Olefin hydrogenation activity

5 Iglesia et al. have shown that both olefins and paraffins are primary products of the FT reaction and that secondary hydrogenation of olefins is an undesired side reaction, because olefins are then prevented from further chain growth. A reduction in olefin hydrogenation activity without decreasing the main hydrocarbon productivity would therefore be a desired catalyst property. However, there is no guidance in the prior art as to how this property shall be implemented into a working catalyst.

10 More detailed analysis of the results from the fixed-bed reactor tests described in Examples 2 and 3 and other supporting tests indeed indicate that the cause of the selectivity improvement of the catalyst according to the invention is associated with a reduced activity for hydrogenation of olefins although a simultaneous reduction in the activity for termination of growing chains by hydrogenation can not be entirely
15 excluded.

These conclusions are based on Figures 7 to 9. Figure 7 shows propene and propane selectivity as a function of support surface area for Co-Re/Al₂O₃ catalysts with particle size < 100 microns ($\chi < 150 \cdot 10^{16} \text{ m}^{-1}$). Co/Re = 20-24, 5-20 wt% Co. These tests
20 were fixed bed reactor tests at: 210°C, 20 bar, H₂/CO = 2.1, 45-55% conversion, about 100 h on stream.

Figure 8 shows the effect of χ on propene selectivity using Al₂O₃ supported cobalt catalysts with different surface area / α - alumina content. In this figure, open symbols
25 represent high surface area γ -alumina support; filled symbols represent low surface area α - alumina support. These tests were fixed bed reactor tests at: 210°C, 20 bar, H₂/CO = 2.1, 40-70% conversion, > 24 h on stream.

Figure 9 shows the effect of χ on propane selectivity using Al_2O_3 supported cobalt catalysts with different surface area / α - alumina content. In this figure, open symbols represent high surface area γ -alumina support; filled symbols represent low surface area α -alumina support. These tests were fixed bed reactor tests at: 210°C, 20 bar, $\text{H}_2/\text{CO} = 2.1$, 40-70% conversion, > 24 h on stream.

Thus, these Figures show decreased light paraffin selectivity for low surface area / high α -alumina supported catalysts and indicate that the activity for olefin hydrogenation is reduced for catalysts according to the invention. (Propene/propane has been selected here as representative of light olefin / paraffin products. Similar effects are observed for other light products). Figure 7 shows that although propene selectivity is reduced for low surface area / high α - alumina supported catalysts, this is not accompanied by an increase in the production of the corresponding paraffin (propane).

A similar effect is observed when χ is increased by increasing particle size (Figures 8 and 9). When χ is increased by increasing the particle size, the olefin (propene) selectivity is continuously decreasing as a result of olefins being converted into secondary products. Propane selectivity starts to increase at a χ - value of about $1000 \times 10^{16} \text{ m}^{-1}$, indicating that light olefins are converted to the corresponding paraffin. This is a result of diffusion resistance on the reactants (H_2 , CO) leading to low CO concentrations in the catalyst pores and thus conditions more favorable for secondary olefin hydrogenation. Although the results show that this reaction can not be blocked totally for the catalysts according to the invention, the tendency for propane formation is lower for all χ - values.

Thus, the present invention describes a way of decreasing the olefin hydrogenation activity of a Fischer - Tropsch catalyst without significantly altering the main hydrocarbon synthesis activity.

In addition to the indirect evidence described above, direct evidence for reduced olefin hydrogenation activity for the catalysts according to the invention was found by performing separate olefin hydrogenation experiments. Selected catalysts prepared and pretreated according to the procedures described in Examples 1 to 2 were tested in a fixed-bed reactor for propene hydrogenation activity. The results are shown in Table 8. The olefin hydrogenation rate for a low surface area/high α -alumina based catalyst is more than a factor of 2 lower than the catalysts included for comparison.

Table 3. Propene hydrogenation activity of 12%Co-0.5%Re / Al₂O₃ with different surface area and phase composition. T = 120°C, P = 1 atm. Feed consisting of 0.2 vol% propene, 1.3 vol% H₂ and balance He (diluent).

Cat.	Surface area (m ² /g)	α - Al ₂ O ₃ (%)	Propane formation rate (g/g cat./h)
2	191	0	1.1
3	66	7	1.1
4	16	86	0.4

Claims

1. A catalyst for use in a Fischer-Tropsch synthesis reaction which comprises cobalt supported on alumina, in which the alumina support has a specific surface area of $<50\text{m}^2/\text{g}$.
5
2. A catalyst for use in a Fischer-Tropsch synthesis reaction which comprises cobalt supported on alumina, in which the alumina support is at least 10% alpha- alumina.
10
3. A catalyst as claimed in Claim 1 and Claim 2.
4. A catalyst as claimed in any preceding Claim, in which the specific surface area of the alumina is $<30\text{m}^2/\text{g}$.
15
5. A catalyst as claimed in any of Claims 2 to 4, in which the alumina is at least 50% and preferably at least 80% alpha-alumina.
6. A catalyst as claimed in Claim 5, in which the alumina is substantially pure alpha-alumina.
20
7. A catalyst as claimed in any preceding Claim, in which the cobalt represents from 3 to 35% by weight of the catalyst.
8. A catalyst as claimed in Claim 7, in which the cobalt represents from 5 to 20% by weight of the catalyst.
25
9. A catalyst as claimed in any preceding Claim, further comprising a promoter.

10. A catalyst as claimed in Claim 9, in which the promoter is rhenium, platinum, rhodium and/or iridium.
- 5 11. A catalyst as claimed in Claim 10, in which the promoter is rhenium and is present as 0.5 to 50% of the cobalt content.
12. A catalyst as claimed in Claim 10, in which the promoter is platinum, rhodium and/or iridium and is present as 0.1 to 50% of the cobalt content.
- 10 13. A catalyst as claimed in Claim 9, comprising up to 2% by weight of the promoter in total.
14. A method of manufacturing a Fischer-Tropsch catalyst which comprises heat treating alumina particles at a temperature in the range 700 to 1300°C for a
15 period of between 1 and 15 hours; and impregnating the heat treated particles with cobalt.
15. A method as claimed in Claim 14, further including the step of impregnating the alumina particles with cobalt, together with a promoter/dopant.
- 20 16. A method as claimed in Claim 15; in which the promoter is rhenium, platinum, iridium and/or rhodium.
17. The use of a catalyst as claimed in any of Claims 1 to 13 in a Fischer-Tropsch
25 synthesis reaction.
18. A use as claimed in Claim 17 in which the reaction is conducted in a slurry bubble column reactor.

19. A method of producing hydrocarbons, in which synthesis gas is reacted in the presence of a catalyst as claimed in any one of claims 1 to 13.
- 5 20. A method as claimed in claim 19, in which the reaction is conducted in a slurry bubble column.
21. A method as claimed in claim 20, in which the reaction temperature is in the range 150 to 300°C
- 10 22. A method as claimed in claim 21, in which the reaction temperature is in the range 175 to 250°C.
23. A method as claimed in any one of claims 20 to 22, in which the reaction pressure is in the range 1 to 100 bar.
- 15 24. A method as claimed in claim 23, in which the reaction pressure is in the range 10 to 50 bar.
- 20 25. A method of converting natural gas to C₅+ hydrocarbons, which comprises; subjecting a natural gas feed stream to a reforming reaction to produce a synthesis gas feed stream of hydrocarbon and carbon monoxide; subjecting the synthesis gas feed stream to a Fischer-Tropsch synthesis reaction in the presence of a catalyst as claimed in any of Claims 1 to 13; and separating a product stream including C₅+ hydrocarbons.

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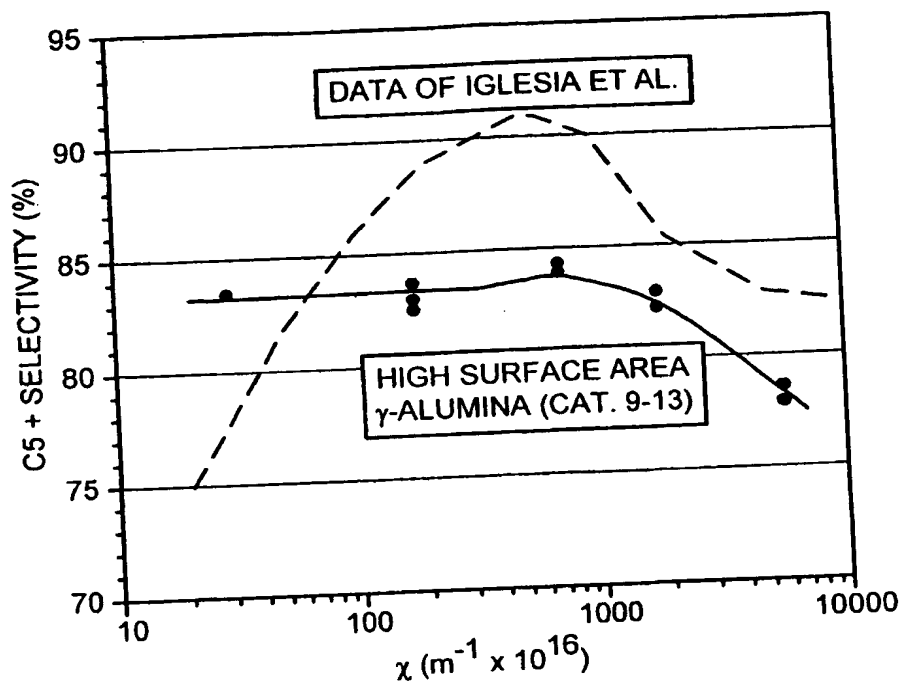


FIG. 1

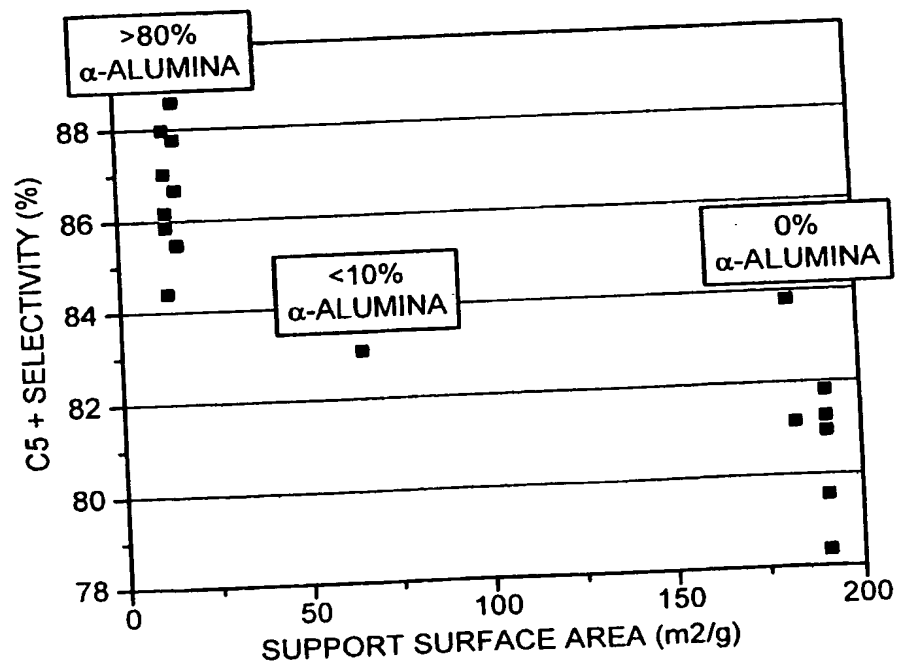


FIG. 2

2 / 5

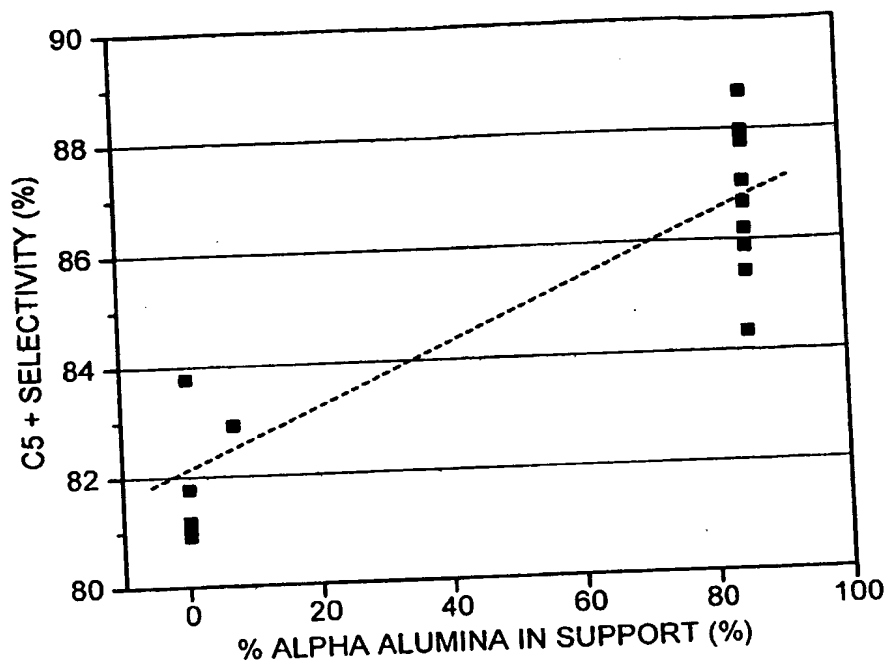


FIG. 3

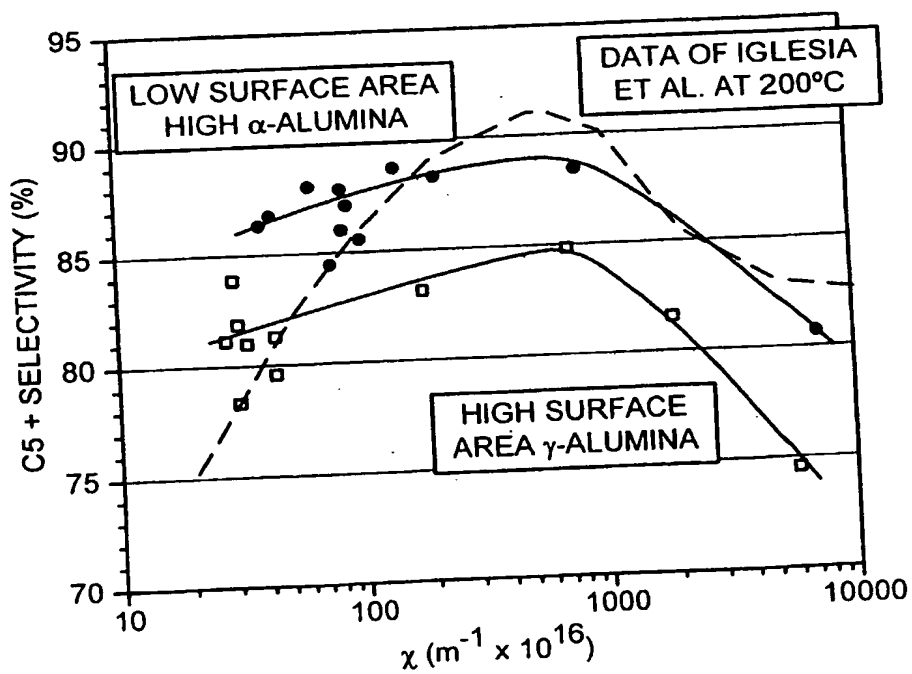


FIG. 4

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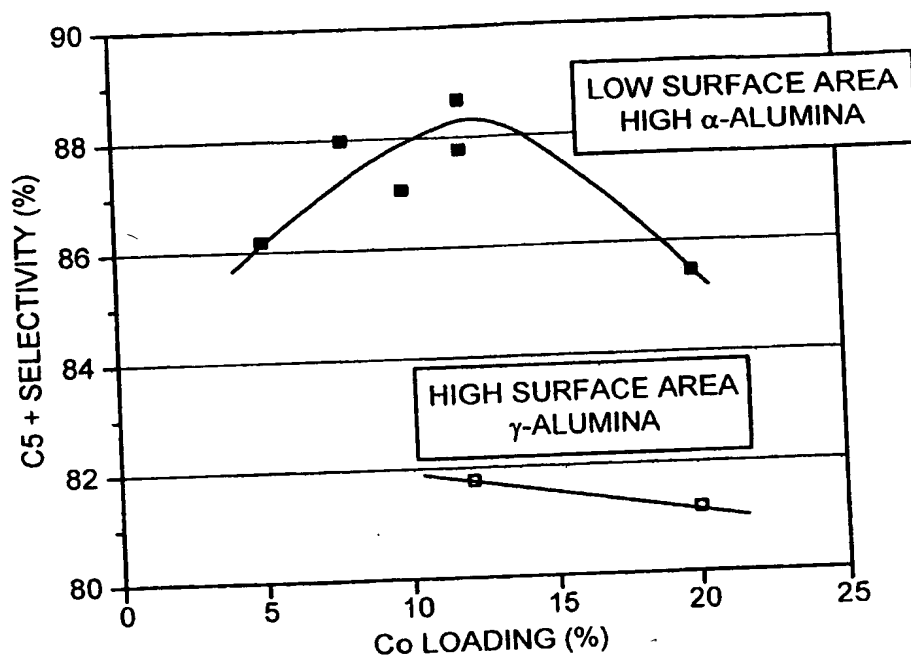


FIG. 5

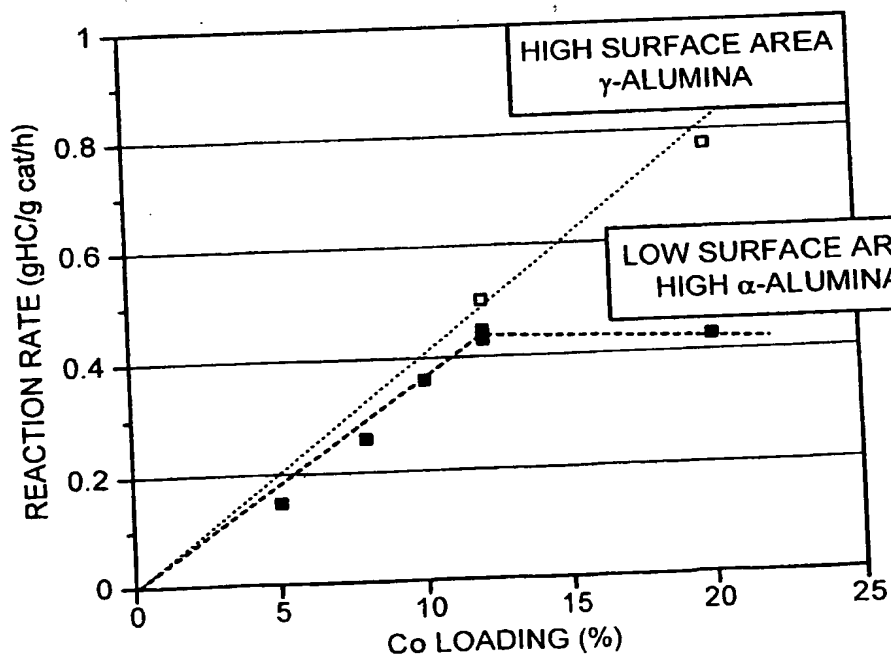


FIG. 6

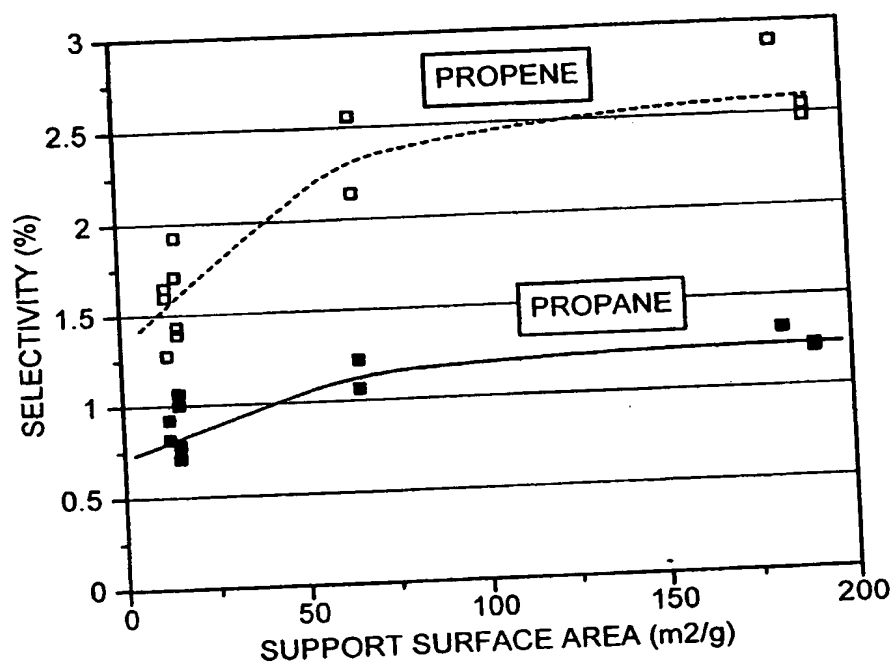


FIG. 7

5/5

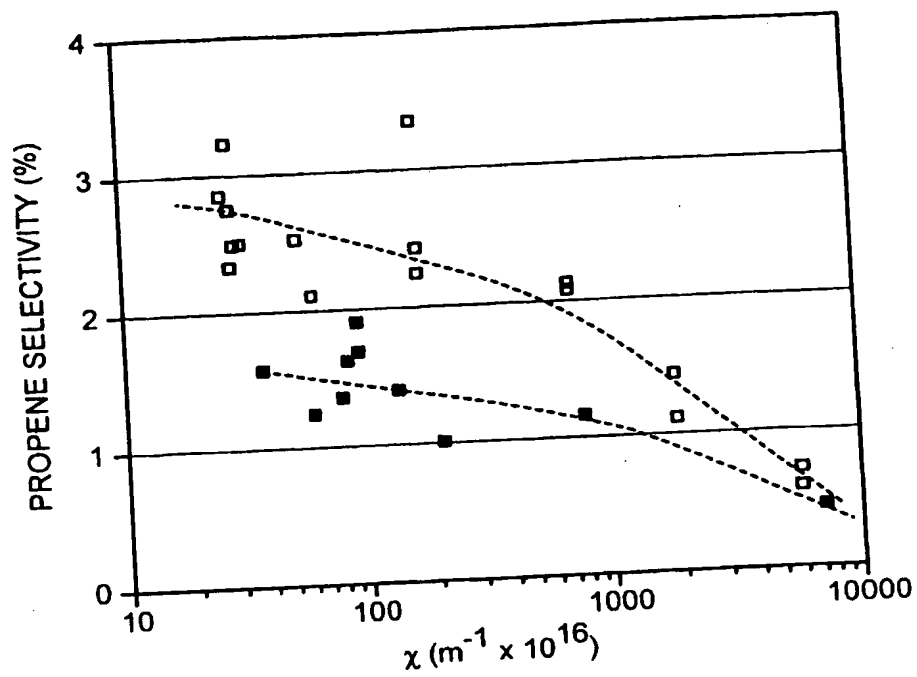


FIG. 8

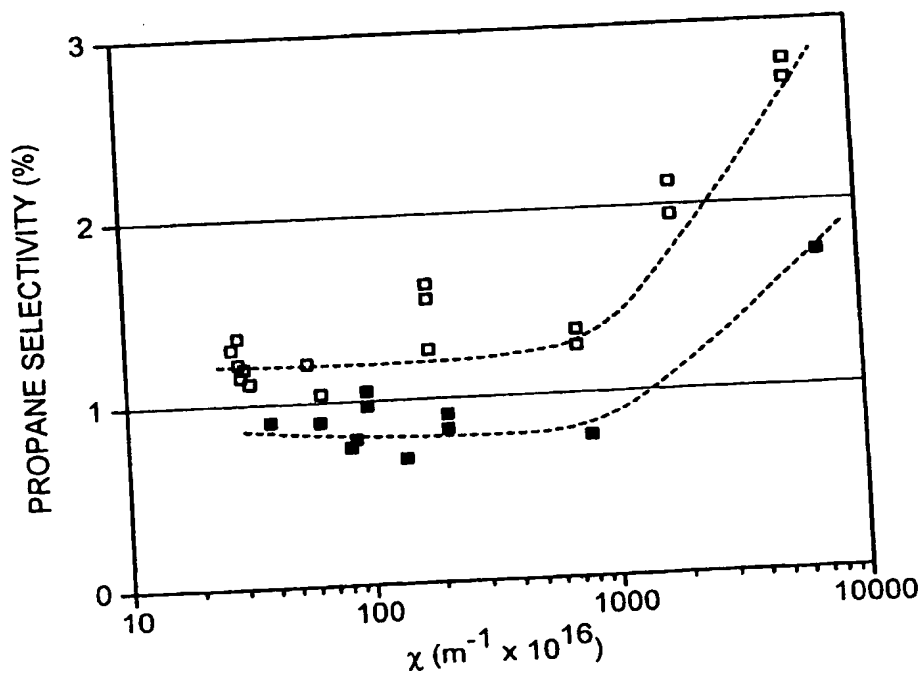


FIG. 9

SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

PCT/GB 01/05461

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J23/75 B01J21/04 B01J35/10 C10G2/00 C07C1/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01J C10G C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 801 620 A (KONDOH SHIROH ET AL) 31 January 1989 (1989-01-31) example 1; tables 1,2 ---	1-7, 17, 19, 25
X	US 2 548 159 A (FREDERIK ENGEL WILLEM ET AL) 10 April 1951 (1951-04-10) the whole document ---	1-9, 13, 17, 19
X	TANG S ET AL: "PARTIAL OXIDATION OF METHANE TO SYNTHESIS GAS OVER ALPHA-AL2O3-SUPPORTED BIMETALLIC PT-CO CATALYSTS" CATALYSIS LETTERS, BALTZER, SCIENTIFIC PUBL, BASEL, CH, vol. 59, no. 2/4, June 1999 (1999-06), pages 129-135, XP000835415 ISSN: 1011-372X	1-10, 12, 13
Y	paragraph 2.1. Preparation of catalysts --- -/-	14-16

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

21 February 2002

Date of mailing of the international search report

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PCT/GB 01/05461

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